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(54) **Cross-linked acrylic copolymers in aqueous emulsion with improved thickening and suspending properties**

(57) Cross-linked copolymers possessing high thickening and suspending properties obtainable by polymerization of monomeric systems comprising a) 10-97% of at least one unsaturated carboxylic acid, b) 0-80% of at least one alkyl ester of an unsaturated acid, c) 0.5-80% of an associative monomer, d) 0-20% of an unsaturated amide, e) 0.2-20% of a suitable cross-linking agent and f) 0-20% of an unsaturated sulfonic acid; processes for their preparation, which comprise polymerization by precipitation, suspension and solution polymerizations or emulsion polymerization; latexes comprising up to 50% or more of said copolymers; said cross-linked copolymers and said latexes whenever prepared by the above polymerization processes; their use as thickening agents of aqueous, or substantially aqueous systems; and the new cross-linking agents.

**EP 0 870 785 A1**

**Description**

The present invention refers to cross-linked copolymers possessing high thickening and suspending properties, their use in aqueous systems and the processes through which these copolymers can be obtained.

Background of the invention

In the literature, including the patent literature, various thickening agents derived from poly(meth)acrylic acid, optionally copolymerized with cross-linkers, are described. As an example, US Patent 2,798,053 reports thickeners known as CARBOPOL<sup>®</sup>, obtained as powders by precipitation of the copolymer from different solvent systems and subsequent drying. However, the handling of volatile powders makes their use problematic and limits their corresponding employment; in addition, the aqueous dispersion of said products reaches high viscosities even at low concentrations, thus hampering their use in the form of stable suspensions.

In British Patent 870,994, the preparation of copolymers of methacrylic acid with alkyl acrylates is described, in which said copolymers are synthesized in concentrated (25-50% of solid content) and fluid aqueous emulsions.

In US Patent 4,138,381, the unsaturated carboxylic acids are copolymerized with alkyl acrylates and with esters between (meth)acrylic acid and polyethoxylated (5-80 moles of ethylene oxide) fatty alcohols (C<sub>0-20</sub>), for the purpose of obtaining a better thickening power and a reduced sensitivity towards the salts present in the solution to be thickened. The polymerization described in this patent is carried out in glycol or in a 50% water-glycol mixture.

EP A1 0013836 reports the copolymerization in aqueous emulsion of (meth)acrylic acid with alkyl acrylates and an ester of (meth)acrylic acid with a (C<sub>8-30</sub>)alkyl, alkylaryl or polycyclic alkyl monoether of a polyethyleneglycol. The polymerization is optionally carried out in the presence of a cross-linking agent, which, however, is employed in quantities never higher than 1%, calculated on the total weight of the monomers. Products are obtained endowed with thickening properties which, in addition, possess an acceptable resistance towards the electrolytes which may be present in the various systems to be thickened.

Similarly, in EP A1 0109820 and EP B1 0217485, cross-linked copolymers are described, which are prepared by polymerization in aqueous emulsion and in which the cross-linking agent, when employed, is again present in quantities which are never higher than 1%, calculated on the total weight of the monomers. Also these copolymers seem to possess a reduced sensitivity towards electrolytes.

EP A1 0658579 reports the preparation of non cross-linked thickening agents deriving from the copolymerization of a monomeric system consisting of, among others, (meth)acrylic acid, an ester of (meth)acrylic acid and an associative monomer which is the sorbate of an O-alkyl-polyoxyethylene glycol.

Finally, in WO 96/35757, aqueous print pastes are described which are thickened by cross-linked copolymers having a particle size higher than 200 nm. These copolymers are obtained by polymerization in aqueous emulsion of a (meth)acrylic acid/(meth)acrylate/allyl-O-PEG-O-alkyl system in the presence of a cross-linking agent which is preferably employed in amounts not higher than 0.05%; it is also represented that, in order to obtain an aqueous print paste possessing improved color yield, the polymerization is advantageously carried out in the presence of ethoxylated alcohol phosphates as surfactants/emulsifiers.

Detailed disclosure of the invention

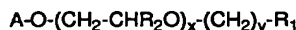
The present invention refers to new cross-linked copolymers showing high thickening and suspending properties, their use in aqueous, or substantially aqueous systems, and the processes by which these copolymers can be obtained.

For example, these processes can be precipitation polymerizations, suspension and solution polymerizations, or emulsion polymerizations of the type oil-in-water or water-in-oil. Preferred is the oil-in-water emulsion polymerization process, through which latexes of the cross-linked copolymers of the invention can be obtained with a solid content up to 50% or more. These latexes, which form a further object of the invention, are easy to be handled (if compared, for example, with the CARBOPOL<sup>®</sup>s, which are powders), remain fluid up to a pH of about 6, and can be employed as such or diluted to a predetermined degree depending on the envisaged use. Thus, when these latexes, or the corresponding diluted emulsions, are added to an aqueous, or substantially aqueous system and, in turn, this is added with an organic or inorganic base, or with a mixture thereof, so as to bring the pH of the system to a pH value higher than about 6, a marked increase of the viscosity of the same system is observed. This feature makes these copolymers useful as thickening and suspending agents for a wide variety of uses, as an example, in the cosmetic and textile industry. In fact, it has surprisingly been found that the copolymers of the present invention possess higher suspending properties in comparison with the art-known copolymers of (meth)acrylic acid, that also the thickening properties of the emulsions according to the invention are higher if compared with those of the art-known polymeric emulsions, and that their thickening properties are not substantially influenced by the presence of electrolytes. Furthermore, the viscosity and the

rheology of the aqueous, or substantially aqueous systems thickened with the cross-linked copolymers of the invention remain substantially unaltered for a long time.

Accordingly, an object of the present invention is represented by cross-linked copolymers obtainable by copolymerization of a monomeric system comprising:

- a) from about 10 to about 97% by weight of at least one ethylenically unsaturated mono- or dicarboxylic acid;
- b) from 0 to about 80% by weight of at least one (C<sub>1-20</sub>)alkyl or aralkyl ester of an ethylenically unsaturated mono- or dicarboxylic acid;
- c) from about 0.5 to about 80% by weight of at least one associative monomer which is an ester of formula



wherein A is an ethylenically unsaturated acyclic residue, optionally containing an additional carboxylic group, wherein, optionally, said additional carboxylic group may be esterified with a (C<sub>1-20</sub>)aliphatic alkyl group;  
 R<sub>1</sub> is an alkyl, alkylphenyl or aralkyl residue having from 1 to 30 carbon atoms;  
 R<sub>2</sub> is hydrogen, methyl or ethyl;  
 x is comprised between 0 and 50;  
 y is comprised between 0 and 30;

- d) from 0 to about 20% by weight of at least one ethylenically unsaturated amide;
- e) from about 0.2 to about 20% by weight of at least one diester between a polyoxyalkyleneglycol or an emulsifier having at least two free OH-groups and an ethylenically unsaturated carboxylic acid, as the cross-linking agent;
- f) from 0 to about 20% by weight of at least one ethylenically unsaturated sulfonic acid.

Examples of ethylenically unsaturated mono- or dicarboxylic acids as indicated under a) are, for example, acrylic, methacrylic, itaconic, maleic, sorbic, crotonic acids, and analogs. Among these, acrylic and methacrylic acids are the preferred ones.

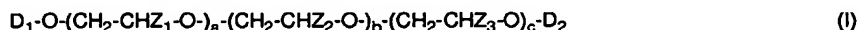
Preferred esters of ethylenically unsaturated mono- or dicarboxylic acids indicated under b) are methyl acrylate, ethyl acrylate, methyl methacrylate, butyl acrylate, ethyl methacrylate and analogs. The most preferred ones are methyl and ethyl (meth)acrylate.

The associative monomer c) may be any compound falling within the above formula A-O-(CH<sub>2</sub>-CH(R<sub>2</sub>)O)<sub>x</sub>-(CH<sub>2</sub>)<sub>y</sub>-R<sub>1</sub> wherein R<sub>1</sub> and R<sub>2</sub> are as above indicated, the sum of x and y may vary between 0 and 80 and A is the acyclic residue of an ethylenically unsaturated acid selected from acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic and linoleic acids. Preferred are the esters of cetylstearylalcohol ethoxylated with 25 moles of ethylene oxide. The associative monomers c) are commercially available products, or they can be prepared substantially according to procedures known in the art (U.S. Patents 3,652,497 and 4,075,411).

The preferred ethylenically unsaturated amides d) are acrylamide, methacrylamide and vinylpyrrolidone, whereas the preferred ethylenically unsaturated sulfonic acids f) are vinylsulfonic acid and p-styrenesulfonic acid.

The cross-linking agents listed under point e) above can have one of the following structures of formula (I), (II) or (IV), or they are polyethoxylated derivatives of castor oil, optionally hydrogenated in whole or in part, esterified with ethylenically unsaturated carboxylic acids, with the proviso that the total number of ethylenic bonds is at least two.

In a first aspect of the present invention, the cross-linking agent e) is a compound of formula (I):



wherein:

D<sub>1</sub> and D<sub>2</sub>, which can be the same or different, are an ethylenically unsaturated acyclic residue, which may contain an additional carboxylic group wherein, optionally, said additional carboxylic group can be esterified with a (C<sub>1-20</sub>)aliphatic alkyl group;

Z<sub>1</sub> and Z<sub>3</sub> represent independently hydrogen or a (C<sub>1-20</sub>) aliphatic alkyl or aralkyl group;

Z<sub>2</sub> is hydrogen or methyl;

a and c are integers comprised between 0 and 20;

b is an integer comprised between 1 and 100;

the sum a+b+c may represent any integer comprised between 1 and 140;

with the proviso that, when Z<sub>1</sub>, Z<sub>2</sub> and Z<sub>3</sub> are simultaneously hydrogen and D<sub>1</sub> and D<sub>2</sub> are simultaneously the acyl residue of methacrylic acid, the sum a+b+c cannot be 1;

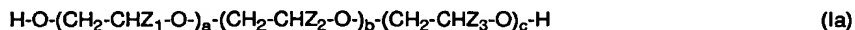
and wherein the structure of the polyalkyleneglycol may be random or block.

Preferably, in the cross-linking agents of formula (I),  $D_1$  and  $D_2$  represent, independently, the acyclic residue of acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic or linoleic acid,  $Z_1$ ,  $Z_2$  and  $Z_3$  represent hydrogen or methyl, the sum  $a+b+c$  is higher than 10 and the structure of the polyalkyleneglycol may be random or block.

More preferably, in the cross-linking agents of formula (I),  $D_1$  and  $D_2$  represent, independently, the acyclic residue of acrylic, methacrylic or itaconic acid,  $Z_1$ ,  $Z_2$  and  $Z_3$  represent hydrogen, and the sum  $a+b+c$  is higher than 20.

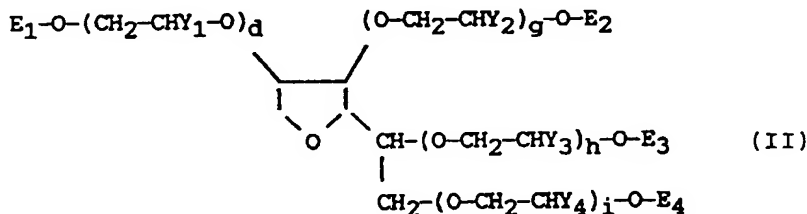
The cross-linking agents of formula (I) are products deriving from the esterification of polyalkyleneglycols with ethylenically unsaturated carboxylic acids; some of them are described in the literature (U.S. Patents 3,639,459, and 4,138,381; DD Patent 205,891; Polymer, 1978, 19(9), 1067-1073; Pigm. Resin. Technol., 1992, 21(5), 16-17).

The compounds of formula (I) can also be prepared by esterification of the compounds of formula (Ia)



wherein  $Z_1$ ,  $Z_2$ ,  $Z_3$ ,  $a$ ,  $b$  and  $c$  are as above defined, with a carboxylic acid  $D_1-OH$  and/or  $D_2-OH$ , wherein  $D_1$  and  $D_2$  are as above defined, or the corresponding anhydride or acyl halide or, alternatively, by trans-esterification of the corresponding esters of low-boiling alcohols.

In a second aspect of the present invention, the cross-linking agent e) is a compound of formula (II)



wherein:

$E_1$ ,  $E_2$ ,  $E_3$  and  $E_4$  represent independently hydrogen or the acyclic residue of a saturated or ethylenically unsaturated mono- or dicarboxylic acid from 2 to 25 carbon atoms, in which the further carboxylic group can optionally be esterified with a  $(C_{1-20})$ aliphatic alkyl group, with the proviso that at least two of  $E_1$ ,  $E_2$ ,  $E_3$  and  $E_4$  represent ethylenically unsaturated acyclic residues as above defined;

$Y_1$ ,  $Y_2$ ,  $Y_3$  and  $Y_4$ , which can be the same or different, are hydrogen, methyl or ethyl;

$d$ ,  $g$ ,  $h$  and  $i$  are integers comprised between 0 and 30.

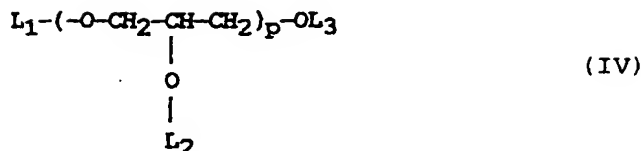
Preferably, the compounds of formula (II) are sorbitan derivatives (all of  $d$ ,  $g$ ,  $h$  and  $i$  are 0) or sorbitan derivatives ethoxylated with from about 4 to about 20 moles of ethylene oxide, in which at least two of the hydroxy groups are esterified with ethylenically unsaturated carboxylic acids selected from acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic and linoleic acids, and at least one of the two residual hydroxy groups is esterified with a fatty acid from 10 to 25 carbon atoms.

The compounds of formula (II) are prepared by introducing the ethylenically unsaturated acyl groups as reported above in the preparation of the compounds of formula (I). The starting substrate is a compound of formula (II) wherein at least two of  $E_1$ ,  $E_2$ ,  $E_3$  and  $E_4$  represent hydrogen, and the remaining of  $E_1$ ,  $E_2$ ,  $E_3$  and  $E_4$  can be hydrogen or an acyl group as above defined.

In a third aspect of the present invention, the cross-linking agent e) is a polyethoxylated derivative of castor oil, optionally partially or totally hydrogenated, esterified with an ethylenically unsaturated carboxylic acid, with the proviso that, in said cross-linking agent, the total number of bonds of ethylenic type is at least two. Preferred are the polyethoxylated derivatives of castor oil with an ethoxylation degree varying from about 15 to about 150, esterified with acids selected from acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic and linoleic acids.

These compounds are prepared by esterification of the corresponding polyethoxylated derivatives of castor oil, optionally partially or totally hydrogenated, following procedures known in the art.

In a fourth aspect of the present invention, the cross-linking agent e) is a compound of formula (IV)

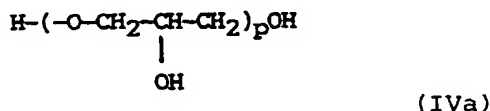


wherein:

L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub>, which may be the same or different, are hydrogen or an acyl residue of a saturated or unsaturated mono- or dicarboxylic acid from 2 to 25 carbon atoms, in which the further carboxylic group can optionally be esterified with a (C<sub>1-20</sub>)aliphatic alkyl group, with the proviso that at least two of L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub> represent an ethylenically unsaturated acyl residue as above defined;  
p is an integer comprised between 2 and 50.

Also in this case, the preferred ethylenically unsaturated acyl residue derive from acids selected from acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic and linoleic acids.

Also the compounds of formula (IV) are prepared through the above illustrated conventional procedures, starting from a polyglycerol of formula (IVa):



Some of these cross-linking agents are new; accordingly, they represent a further object of the present invention.

The above described cross-linking agents have been identified by means of <sup>1</sup>H NMR and <sup>13</sup>C NMR (spectrometer: BRUKER ARX 300). The analysis of the obtained spectra has confirmed that the percentage of the residual OH-groups after the esterification is negligible.

As illustrated above, the amounts in which the cross-linking agents are employed may vary within wide limits. Preferably, amounts of cross-linking agents are used higher than 0.3% of the total weight of the monomers. More preferably, the amounts of cross-linking agents are higher than 1.0% of the total weight of the monomers.

The cross-linked copolymers of the invention can be prepared by different polymerization procedures such as, for instance, the precipitation polymerization, suspension and solution polymerizations, or the emulsion polymerizations of the type oil-in-water or water-in-oil. The conditions of the polymerization reactions are, basically, those known in the art. Generally, the polymerizations are performed in the presence of anionic surfactants/emulsifiers, such as, for instance, sodium dodecylbenzenesulfonate, sodium disecundary-butylphenyl sulfonate, sodium laurylsulfate, sodium lauryl ether sulfate, disodium dodecylphenyl ether disulphonate, disodium n-octadecylsulfosuccinamate or sodium diocetyl sulfosuccinate. Particularly preferred are sodium laurylsulfate and sodium lauryl ether sulfate. The temperature is generally comprised between about 50 and about 120°C, and the polymerization is completed in about 2-8 hours. The most preferred polymerization reaction is the oil-in-water emulsion polymerization.

The invention is further illustrated by the following examples.

#### EXAMPLES A-AC

Examples A-AC, reported in the following, describe the preparation of the cross-linking agents e).

The so obtained cross-linking agents will hereinafter be identified through the letter/s of the relevant preparation, as indicated in Table 1.

Though the esterification products described in the present invention can be obtained by means of different synthetic pathways such as, for instance, the transesterifications or the condensation with acyl halides, the following illustrative examples report direct esterifications with carboxylic acids using, as an example, xylene or n-octane as the solvents, in the presence of acids like 95% sulfuric acids, or esterifications performed with anhydrides, in the absence of solvents and acids.

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The reactions were carried out in a glass reactor equipped with stirrer, thermometer, Dean-Stark apparatus or reflux condenser, depending on whether an acid or an anhydride is used, and diffuser through which air is blown for the whole duration of the reaction, in order to keep active the polymerization inhibitor.

The reactor was charged with:

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1) the precursors to be esterified, namely the compounds of formulae (Ia), (IIa), (IVa), or the polyethoxylated derivatives of castor oil;

2) the ethylenically unsaturated carboxylic acids, or the anhydrides in stoichiometric ratio with the hydroxy groups of the above precursors which one desires to esterify;

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3) 0.5% by weight of sulfuric acid (not employed if the acylation reaction is carried out with anhydrides);

4) 1% by weight of hydroquinone monomethylether as the polymerization inhibitor;

said weight percentages being calculated on the total weight of the solids, and

5) an amount of solvent (xylene or n-octane, not employed if the acylation reaction is carried out with anhydrides) so as to have a weight per cent content of solids of 30.

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The reaction mixture was refluxed until complete elimination of the water, in the presence of a steady air bubbling, in order to avoid the deactivation of the hydroquinone monomethylether (the polymerization inhibitor). Once the polymerization was terminated, the solvent was distilled off *in vacuo*, thus leaving a waxy product, pourable upon heating, which was employed as such in the subsequent polymerizations.

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Table 1 lists the so obtained cross-linking agents e). In this Table, PEG means polyethylene glycol and the number which follows represents its average molecular weight; PLURONIC<sup>®</sup> L122, F-68 and 63N10 are copolymers of polyethylene and polypropylene glycols; PPG stands for polypropylene glycol and the number which follows represents its average molecular weight; "c. oil" means castor oil, where the number followed by EO represents the number of condensed moles of ethylene oxide per mole of starting castor oil; TWEEN<sup>®</sup> 80 (I.C.I.) is sorbitan monooleate ethoxylated with 20 moles of ethylene oxide; ELFACOS<sup>®</sup> (Akzo-Nobel) is a block copolymer of ethylene oxide with two blocks of polydodecylglycol; EMCOL<sup>®</sup> 14 is a polyglyceryl-4 oleate (Witco), monoester of oleic acid with tetraglycerol.

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Table 1 - Syntheses of the cross-linking agents e)

Esterification of PEG 1000				
Preparation	Precursor	Unsaturated acid or anhydride	Solvent	Acid
A	PEG1000	Acrylic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>
B	PEG1000	Maleic anhydride	---	---
C	PEG1000	Methacrylic anhydride	---	---
D	PEG1000	Methacrylic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>
Esterification of PEGs with different average molecular weight				
E	PEG 1000	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>
F	PEG 2000	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>
G	PEG 3000	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>
H	PEG 12000	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>
I	PLURONIC L122	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>
J	PLURONIC F-68	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>
K	PLURONIC 63N10	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>
L	PPG 600	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>



Table 1 - follows

## Esterification of copolymers PEG/dodecylglycols (ELFACOS®)

M	ELFACOS ST37	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	(I)
N	ELFACOS ST37	Acrylic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	(I)
Esterification of castor oil 57EO					
O	C.oil 57EO	Sorbic acid	Xylene	95% H <sub>2</sub> SO <sub>4</sub>	C. oil 57EO di- and trisorbate
P	C.oil 57EO	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	C. oil 57EO di- and tritaconate
Q	C.oil 57EO	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	do
R	C.oil 57EO	Acrylic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	C. oil 57EO di- and triacrylate
S	C.oil 57EO	Maleic anhydride	---	---	C. oil 57EO di- and trimaleate

Table 1 - follows

## Esterification of TWEEN®

T	TWEEN 80	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	(II)
U	TWEEN 80	Acrylic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	(II)
V	TWEEN 20	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	(II)
W	TWEEN 20	Acrylic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	(II)

## Esterification of castor oil with different ethoxylation degrees

X	C. oil 30EO	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	C. oil 30EO di- and triitaconate
Y	C. oil 80EO	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	C. oil 80EO di- and triitaconate

## Esterification of EMCOL® 14

Z	EMCOL 14	Acrylic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	(IV)
AA	EMCOL 14	Itaconic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	(IV)
AB	EMCOL 14	Methacrylic acid	n-octane	95% H <sub>2</sub> SO <sub>4</sub>	(IV)
AC	EMCOL 14	Maleic anhydride	---	---	(IV)

**EXAMPLES 1-4** - Comparative examples

The following examples refer to preparations described in EP A1 0013836, 0109820 and 0658579; they were carried out to compare the art known copolymers with those of the present invention.

5 A 2 liter glass reactor, equipped with stirrer, reflux condenser, thermometer and thermostated bath, was charged with 336.6 ml of deionized water, then nitrogen was bubbled for 30 minutes. Under nitrogen stream, the reactor was subsequently charged with 6.6 g of an aqueous 28% by weight solution of sodium laurylsulfate and 18.725 ml of a monomeric emulsion composed of 127.6 g of deionized water, 126.8 g of ethyl acrylate, 92.7 g of methacrylic acid, 6.6 g of an aqueous 28% by weight solution of sodium laurylsulfate, 36 ml of a 0.7% by weight solution of ammonium persulfate and 24.3 g of the associative monomer c), which is cetylstearyl alcohol ethoxylated with 25 moles of ethylene oxide [identified in the following Table 2 as (C<sub>16-18</sub>)alcohol 25OE] esterified with an acid selected from acrylic, methacrylic, itaconic and sorbic acid, respectively. The temperature was brought to 85°C and kept at this value for 20 minutes, then the remainder of the monomeric emulsion and 20 ml of a 0.7% by weight solution of ammonium persulfate were added over 180 minutes, while keeping the temperature at 85°C. The so obtained acrylic emulsion was cooled and discharged from the reactor.

To evaluate the thickening and suspending properties of the so obtained non cross-linked copolymers, a 1.5% solution of the selected copolymer was neutralized with an aqueous 10% by weight solution of sodium hydroxide. The thickening properties of the so obtained gels were determined with a Brookfield viscosimeter (spindle RV7, T: 20°C); the suspending properties, expressed as "yield value", were determined by difference of the viscosities measured at 1 rpm and 0.5 rpm, divided by 100.

Table 2 reports the results obtained with the four preparations.

Table 2

Preparation	Associative monomer c)	Viscosity 20 rpm*, Cps	Yield value
1	(C <sub>16-18</sub> )alcohol 25OE acrylate	50000	2950
2	(C <sub>16-18</sub> )alcohol 25OE methacrylate	51000	2750
3	(C <sub>16-18</sub> )alcohol 25OE itaconate	48000	2800
4	(C <sub>16-18</sub> )alcohol 25OE sorbate	50000	2800
rpm*: rounds per minute Cps: centipoises			

**Examples 5-50**

The cross-linked copolymers of the present invention were prepared by operating as described in Examples 1-4, in the presence of the cross-linking agent e) and, optionally, of the monomers d) and/or f).

40 A 2 liter glass reactor, equipped with stirrer, reflux condenser, thermometer and thermostated bath was charged with 336.6 ml of deionized water, then nitrogen was bubbled for 30 minutes. Under nitrogen stream, the reactor was subsequently charged with 6.6 g of an aqueous 28% by weight solution of sodium laurylsulfate and 18.725 ml of a monomeric emulsion composed of 127.6 g of deionized water, 219.5 g of the monomers previously described under points a), b), d) and f) in the reciprocal per cent composition described in the following Table, 6.6 g of an aqueous 28% by weight solution of sodium laurylsulfate, 36 ml of a 0.7% by weight solution of ammonium persulfate and 24.3 g of the associative monomer c), which is cetylstearyl alcohol ethoxylated with 25 moles of ethylene oxide [again identified in the following Table 3 as (C<sub>16-18</sub>)alcohol 25OE] esterified with an acid selected from acrylic, methacrylic, itaconic and sorbic acid, and an amount of cross-linking agent e) selected from those previously mentioned in Table 1 under Examples A-AC, as indicated in Table 3. The temperature was brought to 85°C and kept at this value for 20 minutes, then the remainder of the monomeric emulsion and 20 ml of a 0.7% by weight solution of ammonium persulfate were added over 180 minutes, while keeping the temperature at 85°C. The so obtained acrylic emulsion was cooled and discharged from the reactor.

To evaluate the thickening and suspending properties of the so obtained cross-linked copolymers in aqueous systems, a 1.5% solution of the selected copolymer was neutralized with an aqueous 10% by weight solution of sodium hydroxide. The thickening and suspending properties, the latter again expressed as "yield value", of the cross-linked copolymers of the invention were determined as above illustrated in Examples 1-4.

The following Table 3 reports the obtained results.

In this Table, the term "cross-linking agent" means a component e) which is identified through the alphabet letter/s

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as in Table 1, the "component c)" is cetylstearyl alcohol esterified as indicated in Table 3, "monomer composition" represents the employed mixture of monomers referred to under points a), b), d) and f) above, where:

EA stands for ethyl acrylate [component b)];

5 MAA stands for methacrylic acid [component a)];

VP stands for vinylpyrrolidone [component d)];

MAAm stands for methacrylamide [component f)];

and the numbers which follow said acronyms indicate the reciprocal weight percentages of the employed monomers in the "monomer composition". As an example, EA/MAA 60/40 means that the monomer composition comprises 60% by weight of ethyl acrylate and 40% by weight of methacrylic acid.

10 In any case, the amounts of the single components which are employed fall within the above indicated percentages, namely those which refer to the composition of the monomeric system adopted for preparing the copolymer of the present invention.

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Table 3

Copolymer of Ex.	Cross- linking agent e) (grams)	Component c)	Monomer composition (components a, b, d, f)	Viscosity (cps, 20 rpm)	Yield value
5	P (15)	(C <sub>16-18</sub> )alcohol 250E sorbate	EA/MAA 60/40	52000	3300
6	P (15)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	60000	5200
7	R (15)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	66000	4400
8	P (15)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA/MAAm 55/40/5	53000	4000
9	P (15)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA/VP 55/40/5	65000	5400
10	P (15)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA/VSA 55/43/2	52000	4100
11	L (3)	(C <sub>16-18</sub> )alcohol 250E itaconate	EA/MAA 60/40	70000	6400
12	A (4,5)	(C <sub>16-18</sub> )alcohol 250E itaconate	EA/MAA 60/40	64000	5600
13	B (6)	(C <sub>16-18</sub> )alcohol 250E itaconate	EA/MAA 60/40	56000	4000
14	A (4)	(C <sub>16-18</sub> )alcohol 250E methacrylate	EA/MAA 60/40	67000	4400
15	C (5)	(C <sub>16-18</sub> )alcohol 250E methacrylate	EA/MAA 60/40	60000	5000
16	A (4)	(C <sub>16-18</sub> )alcohol 250E methacrylate	EA/MAA/MAAm 55/40/5	62500	4500

Table 3 - follows

17	D (4)	(C <sub>16-18</sub> )alcohol 250E methacrylate	EA/MAA 60/40	60000	5000
18	A (4)	(C <sub>16-18</sub> )alcohol 250E methacrylate	EA/MAA/VP 55/40/5	65000	5400
19	A (4)	(C <sub>16-18</sub> )alcohol 250E methacrylate	EA/MAA/VSA 55/43/2	62000	4500
20	G (8)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	58000	5000
21	A (4)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	69000	6400
22	A (3.3)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 50/50	60000	6000
23	F (6)	(C <sub>16-18</sub> )alcohol 250E itaconate	EA/MAA 60/40	62000	6000
24	E (3.4)	(C <sub>16-18</sub> )alcohol 250E itaconate	EA/MAA/VP 55/40/5	58000	5000
25	E (4.0)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA/VP 53/39/8	55000	4500
26	T (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA/MAAm 55/40/5	56000	5000
27	F (4)	(C <sub>16-18</sub> )alcohol 250E itaconate	EA/MAA 60/40	60000	5800
28	T (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA/VP 55/40/5	54000	4800
29	T (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA/VSA 55/43/2	53000	4800
30	T (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	52000	4000
31	U (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	54000	4500
32	V (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	53500	4200
33	W (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	58000	4800

Table 3 - follows

34	I (6)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	53000	3500
35	J (8)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	64000	4200
36	F (5)	(C <sub>16-18</sub> )alcohol 250E itaconate	EA/MAA 60/40	60000	5700
37	E (4)	(C <sub>16-18</sub> )alcohol 250E itaconate	EA/MAA 60/40	50000	5200
38	E (4.5)	(C <sub>16-18</sub> )alcohol 250E itaconate	EA/MAA 60/40	60000	5600
39	E (4.5)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	55000	5000
40	K (8)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	62000	4100
41	K (8)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA/MAAM 55/40/5	64000	5800
42	K (8)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA/VP 55/40/5	65000	5800
43	K (8)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA/VSA 55/43/2	58000	4300
44	M (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	52000	4500
45	N (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	51500	4200
46	Z (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	56000	4800
47	AA (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	56000	6000
48	AB (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	55000	4100
49	AC (10)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	60000	4900
50	Q (11.5)	(C <sub>16-18</sub> )alcohol 250E acrylate	EA/MAA 60/40	44000	3800

The cross-linked copolymers of the present invention are useful thickening agents of aqueous, or substantially aqueous systems in a variety of fields such as, for instance, the cosmetic and textile industry. In addition, owing to their excellent suspending properties in comparison with those of the corresponding non cross-linked products, aqueous

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based cosmetic compositions can be formulated in which the rheology remains substantially unchanged after a long period of time, or aqueous based print pastes can be prepared having a satisfactory color yield, even when small amounts of said compounds are employed. These thickened compositions represent a further object of the present invention.

5 The following examples report the preparation of cosmetic compositions and printing pastes thickened with representative cross-linked copolymers of the present invention.

### Example A

10 A thickened oil-in-water facial cream is prepared by (the indicated percentages are by weight):

15	1.	Cetearyl polyglucose	3.00%
	2.	Glyceryl stearate	1.00%
	3.	Cetearyl alcohol	1.00%
	4.	Coco caprylate/caprate	5.00%
20	5.	Isopropyl palmitate	5.00%
	6.	Dioctyl ether	5.00%
	7.	Shea butter	2.00%
	8.	Tocopheryl acetate	1.00%
25	9.	Antioxydant	0.05%
	10.	Demineralized water	q.s.to 100%
	11.	Laureth-4 phosphate	0.50%
30	12.	Imidazolydinyl urea	0.30%
	13.	Methylparaben	0.20%
	14.	Propylparaben	0.10%
35	15.	Butylene glycol	2.00%
	16.	Perfume	0.20%
	17.	Thickening agent	1.00%
40	18.	Sodium hydroxide (10% sol.)	q.s.to pH 6.5

The blend of the components 1--->9 is heated at 70°C (phase A). Separately, the water is heated at 70°C and added with the component 11 (phase B). Phase A is added to phase B and the resulting mixture is homogenized. After cooling to 40°C, the mixture is added with the emulsion of the components 12--->15 and with the perfume. After subsequent cooling to room temperature, the thickening agent 17 is added under slow stirring, and the mixture is finally neutralized with component 18.

Thickened oil-in-water facial creams were prepared by using as the thickening agents the cross-linked copolymers of Examples 10, 12, 14, 21, 22, 27, 36 and 38. It was found that the viscosity and the rheology of the so prepared facial creams remained substantially unchanged for several weeks. On the other hand, an identical cream thickened with the non cross-linked copolymer of Example 3 tended to increase its viscosity along the time, to become sticky and lose its homogeneity upon manipulation.

### Example B

55 A thickened eye contour gel is prepared by (the indicated percentages are by weight):



1.	Demineralized water	q.s.to 100%
2.	Imidazolidinyl urea	0.30%
3.	Methyl paraben	0.20%
4.	Thickening agent	3.00%
5.	Sodium hydroxide (10% sol.)	q.s to pH 7.0
6.	PEG-400	1.00%
7.	Panthenol	1.00%
8.	Saccharide Isomerate	2.00%
9.	PEG-35 castor oil and guaiazulene	0.10%

The components 2 and 3 are dissolved in water at room temperature, then the thickening agent 4 is added under slow stirring and the resulting mixture is neutralized with 5. The so obtained gel is added with the mixture of components 6--->9, and the whole is stirred to homogeneity.

Thickened eye contour gels were prepared by using as the thickening agents the cross-linked copolymers of Examples 10, 12, 14, 21, 22, 27, 36 and 38. It was found that the viscosity and the rheology of the so prepared gels remained substantially unchanged for several weeks. On the other hand, an identical eye contour gel thickened with the non cross-linked copolymer of Example 3 tended to increase its viscosity along the time, to become sticky and loose its homogeneity upon manipulation.

#### Example C

A hair fixative gel is prepared by (the indicated percentages are by weight):

1)	Demineralized water	q.s. to 100%
2)	Thickening agent	4.00%
3)	Imidazolidinyl urea	0.30%
4)	Methylparaben	0.20%
5)	Sodium hydroxide (10% sol.)	q.s. to pH 7.0
6)	Ethyl alcohol 95%	3.00
7)	PVP	2.00%
8)	Glycerin	1.00%
9)	Panthenol	1.00%
10)	PEG20 glyceryl ricinoleate and ricinoleamide DEA	0.70%
11)	Perfume	0.20%

Components 3 and 4 are dissolved in water at room temperature, then the thickening agent is added under slow stirring and the whole is neutralized with component 5. Separately, component 7 is dissolved in component 6 and the resulting blend is added to the previously formed gel. The mixture is added with components 8 and 9 and, finally, with the blend of components 10 and 11. Similar results as those obtained in Examples A and B were achieved also with this cosmetic preparation.

**Example D**

Preparation of a print paste.

5 An aqueous based print paste was prepared by (the indicated percentages are by weight):

10	1)	Demineralized water	81.00%
	2)	Defoprint A (silicon defoamer)	0.002%
	3)	Ammonia (25% solution)	0.006%
	4)	Legoprint AN (acrylic binder)	0.110%
15	5)	Fixol ST (color fixing agent)	0.009%
	6)	BLU HELIZARIN® RT (color pigment)	0.030%
	7)	Thickening agent	0.031%

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Components 1, 4 and 5 are commercial products sold by 3V SIGMA S.p.A., Bergamo, Italy.

Tests were carried out by flat and rotatory printing on different fibers (hydrophilic cotton, partially hydrophilic cotton, polyester/ cotton : 50/50 mixture), and using, as the thickening agents, the cross-linked copolymers of Examples 6, 8, 9, 24 and 50. In all cases, the achieved color yields were absolutely satisfactory.

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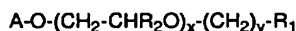
**Claims**

1. Cross-linked copolymers obtainable by copolymerization of a monomeric system comprising:

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- a) from about 10 to about 97% by weight of at least one ethylenically unsaturated mono- or dicarboxylic acid;
- b) from 0 to about 80% by weight of at least one (C<sub>1-20</sub>)alkyl or aralkyl ester of an ethylenically unsaturated mono- or dicarboxylic acid;
- c) from about 0.5 to about 80% by weight of at least one associative monomer which is an ester of formula

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wherein A is an ethylenically unsaturated acyclic residue, optionally containing an additional carboxylic group, wherein, optionally, said additional carboxylic group may be esterified with a (C<sub>1-20</sub>)aliphatic alkyl group;

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R<sub>1</sub> is an alkyl, alkylphenyl or aralkyl residue having from 1 to 30 carbon atoms;

R<sub>2</sub> is hydrogen, methyl or ethyl;

x is comprised between 0 and 50;

y is comprised between 0 and 30;

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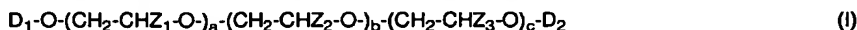
d) from 0 to about 20% by weight of at least one ethylenically unsaturated amide;

e) from about 0.2 to about 20% by weight of at least one diester between a polyoxyalkyleneglycol or an emulsifier having at least two free OH-groups and an ethylenically unsaturated carboxylic acid, as the cross-linking agent;

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f) from 0 to about 20% by weight of at least one ethylenically unsaturated sulfonic acid.

2. Cross-linked copolymers as defined in claim 1, wherein the cross-linking agent e) is a compound of formula (I):



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wherein:

D<sub>1</sub> and D<sub>2</sub>, which can be the same or different, are an ethylenically unsaturated acyclic residue, which may contain an additional carboxylic group wherein, optionally, said additional carboxylic group can be esterified with a

(C<sub>1-20</sub>)aliphatic alkyl group;

Z<sub>1</sub> and Z<sub>3</sub> represent independently hydrogen or a (C<sub>1-20</sub>) aliphatic alkyl or aralkyl group;

Z<sub>2</sub> is hydrogen or methyl;

a and c are integers comprised between 0 and 20;

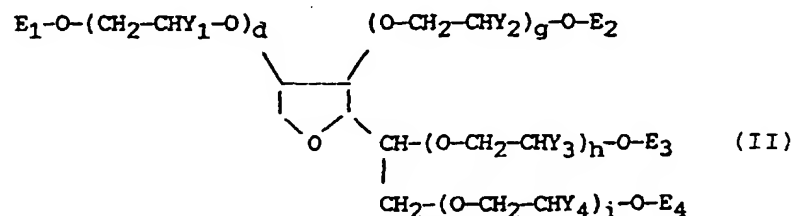
b is an integer comprised between 1 and 100;

the sum a+b+c may represent any integer comprised between 1 and 140;

with the proviso that, when Z<sub>1</sub>, Z<sub>2</sub> and Z<sub>3</sub> are simultaneously hydrogen and D<sub>1</sub> and D<sub>2</sub> are simultaneously the acyl residue of methacrylic acid, the sum a+b+c cannot be 1;

and wherein the structure of the polyalkyleneglycol may be random or block.

3. Cross-linked copolymers as defined in claim 2, wherein D<sub>1</sub> and D<sub>2</sub> represent, independently, the acylic residue of acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic or linoleic acid, Z<sub>1</sub>, Z<sub>2</sub> and Z<sub>3</sub> represent hydrogen or methyl, the sum a+b+c is higher than 10 and the structure of the polyalkyleneglycol may be random or block.
4. Cross-linked copolymers as defined in claim 2, wherein D<sub>1</sub> and D<sub>2</sub> represent, independently, the acylic residue of acrylic, methacrylic or itaconic acid, Z<sub>1</sub>, Z<sub>2</sub> and Z<sub>3</sub> represent hydrogen, and the sum a+b+c is higher than 20.
5. Cross-linked copolymers as defined in claim 1, wherein the cross-linking agent e) is a compound of formula (II):



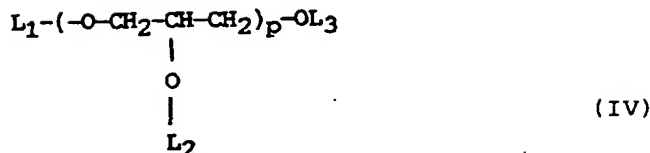
wherein:

E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub> and E<sub>4</sub> represent independently hydrogen or the acylic residue of a saturated or ethylenically unsaturated mono- or dicarboxylic acid from 2 to 25 carbon atoms, in which the further carboxylic group can optionally be esterified with a (C<sub>1-20</sub>)aliphatic alkyl group, with the proviso that at least two of E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub> and E<sub>4</sub> represent ethylenically unsaturated acylic residues as above defined;

Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub>, which can be the same or different, are hydrogen, methyl or ethyl;

d, g, h and i are integers comprised between 0 and 30.

6. Cross-linked copolymers as defined in claim 5, wherein the compounds of formula (II) are sorbitan derivatives or sorbitan derivatives ethoxylated with from about 4 to about 20 moles of ethylene oxide, in which at least two of the hydroxy groups are esterified with ethylenically unsaturated carboxylic acids selected from acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic and linoleic acids, and at least one of the two residual hydroxy groups is esterified with a fatty acid from 10 to 25 carbon atoms.
7. Cross-linked copolymers as defined in claim 1, wherein the cross-linking agent e) is a polyethoxylated derivative of castor oil, optionally partially or totally hydrogenated, esterified with an ethylenically unsaturated carboxylic acid, with the proviso that, in said cross-linking agent, the total number of bonds of ethylenic type is at least two.
8. Cross-linked copolymers as defined in claim 7, wherein the polyethoxylated derivative of castor oil has an ethoxylation degree varying from about 15 to about 150 and is esterified with acids selected from acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic and linoleic acids.
9. Cross-linked copolymers as defined in claim 1, wherein the cross-linking agent e) is a compound of formula (IV)



wherein:

L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub>, which may be the same or different, are hydrogen or an acyl residue of a saturated or unsaturated mono- or dicarboxylic acid from 2 to 25 carbon atoms, in which the further carboxylic group can optionally be esterified with a (C<sub>1-20</sub>)aliphatic alkyl group, with the proviso that at least two of L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub> represent an ethylenically unsaturated acylic residue as above defined;  
p is an integer comprised between 2 and 50.

10. Cross-linked copolymers as defined in claim 9, wherein L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub>, which may be the same or different, represent independently the ethylenically unsaturated acyl residue of acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic and linoleic acids.
11. Cross-linked copolymers as defined in claim 1, wherein the component a) of the monomeric mixture is an ethylenically unsaturated carboxylic acid selected from acrylic, methacrylic, itaconic, maleic, sorbic and crotonic acids.
12. Cross-linked copolymers as defined in claim 1, wherein the component b) of the monomeric mixture is an ester selected from methyl acrylate, ethyl acrylate, methyl methacrylate, butyl acrylate and ethyl methacrylate.
13. Cross-linked copolymers as defined in claim 12, wherein the component b) of the monomeric mixture is an ester selected from methyl acrylate, ethyl acrylate, methyl methacrylate and ethyl methacrylate.
14. Cross-linked copolymers as defined in claim 1, wherein, in the associative monomer c), R<sub>1</sub> and R<sub>2</sub> are as above indicated, the sum of x and y may vary between 0 and 80 and A is the acylic residue of an ethylenically unsaturated acid selected from acrylic, methacrylic, itaconic, maleic, sorbic, crotonic, oleic and linoleic acids.
15. Cross-linked copolymers as defined in claim 14, wherein the associative monomer c) is selected from esters of the ethylenically unsaturated acids defined in claim 14 with cetyl stearyl alcohol ethoxylated with 25 moles of ethylene oxide.
16. Cross-linked copolymers as defined in claim 1, wherein the component d) of the monomeric mixture is an ethylenically unsaturated amide selected from acrylamide, methacrylamide and vinylpyrrolidone.
17. Cross-linked copolymers as defined in claim 1, wherein the component f) of the monomeric mixture is selected from vinylsulfonic acid and p-styrene sulfonic acid.
18. Cross-linked copolymers as defined in any of claims 1-17, in which the cross-linking agent e) is used in amounts higher than 0.3% of the total weight of the monomers of the monomeric system.
19. Cross-linked copolymers as defined in claim 18, in which the cross-linking agent e) is used in amounts higher than 1% of the total weight of the monomers of the monomeric system.
20. Process for preparing the cross-linked copolymers as defined in any of claims 1-19, comprising the precipitation polymerization.
21. Process for preparing the cross-linked copolymers as defined in any of claims 1-19, comprising the suspension polymerization.
22. Process for preparing the cross-linked copolymers as defined in any of claims 1-19, comprising the solution polym-

erization.

23. Process for preparing the cross-linked copolymers as defined in any of claims 1-19, comprising the emulsion polymerization of the type oil-in-water or water-in oil.

24. A process as defined in any of claims 20-23, characterized in that it is carried out in the presence of surfactants/emulsifiers selected from sodium dodecylbenzenesulfonate, sodium disecundary-butynaphthalene sulfonate, sodium laurylsulfate, sodium laurylether sulfate, disodium dodecyldiphenyl ether disulphonate, disodium n-octadecylsulfosuccinamate or sodium dioctylsulfosuccinate.

25. A process as defined in claim 24, in which the surfactants/emulsifiers are selected from sodium laurylsulfate and sodium laurylether sulfate

26. Latexes comprising up to 50% or more of the cross-linked copolymers as defined in any of claims 1-19.

27. Cross-linked copolymers as defined in any of claims 1-19, whenever prepared by a polymerization process as defined in any of claims 20-25.

28. Latexes as defined in claim 26, whenever prepared by a polymerization process as defined in any of claims 23-25.

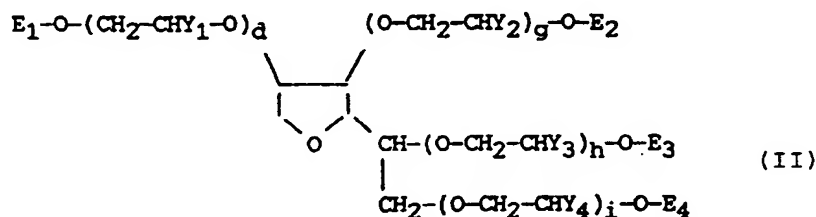
29. The use of the cross-linked copolymers as defined in any of claims 1-19 or 27, or of the latexes as defined in claims 26 or 28 as thickening agents of aqueous, or substantially aqueous systems.

30. The use as defined in claim 29 wherein the aqueous, or substantially aqueous system is a cosmetic or a print paste formulations.

31. A method for increasing the viscosity of an aqueous, or substantially aqueous system which comprises first adding to said aqueous, or substantially aqueous system, at least one cross-linked copolymer as defined in any of claims 1-19 or 27, or at least one latex as defined in claims 26 or 28, and then adding an organic or inorganic base, or a mixture thereof, in order to bring the pH of the system to a value higher than about 6.

32. Aqueous, or substantially aqueous compositions thickened with at least one cross-linked copolymer as defined in any of claims 1-19 or 27, or with a latex as defined in claims 26 or 28.

33. Compounds of formula (II)



wherein:

E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub> and E<sub>4</sub> represent independently hydrogen or the acyclic residue of a saturated or ethylenically unsaturated mono- or dicarboxylic acid from 2 to 25 carbon atoms, in which the further carboxylic group can optionally be esterified with a (C<sub>1-20</sub>)aliphatic alkyl group, with the proviso that at least two of E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub> and E<sub>4</sub> represent ethylenically unsaturated acyclic residues as above defined;

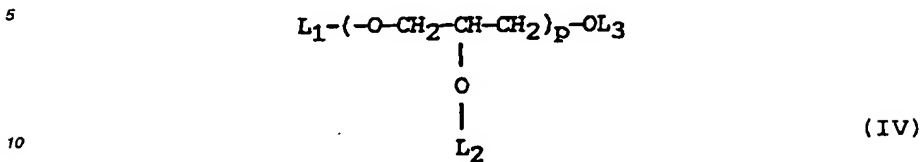
Y<sub>1</sub>, Y<sub>2</sub>, Y<sub>3</sub> and Y<sub>4</sub>, which can be the same or different, are hydrogen, methyl or ethyl;

d, g, h and i are integers comprised between 0 and 30.

34. A cross-linking agent e), which is a polyethoxoylated derivative of castor oil, optionally partially or totally hydrogenated, esterified with an ethylenically unsaturated carboxylic acid, with the proviso that, in said cross-linking agent

e), the total number of bonds of ethylenic type is at least two.

35. Compounds of formula (IV)



wherein:

L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub>, which may be the same or different, are hydrogen or an acyl residue of a saturated or unsaturated mono- or dicarboxylic acid from 2 to 25 carbon atoms, in which the further carboxylic group can optionally be esterified with a (C<sub>1-20</sub>) aliphatic alkyl group, with the proviso that at least two of L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub> represent an ethylenically unsaturated acyclic residue as above defined;  
p is an integer comprised between 2 and 50.



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## EUROPEAN SEARCH REPORT

Application Number  
EP 98 10 6096

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	EP 0 013 836 A (ROHM AND HAAS CO.) 6 August 1980 ---		C08F220/04 C08F220/28 C09D7/00
A	EP 0 238 404 A (MAN. DE PRODUITS CHIMIQUES PROTEX) 23 September 1987 ---		
D,A	US 4 138 381 A (D. CHANG) 6 February 1979 -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 July 1998	Examiner Cauwenberg, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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